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Patent

Attorney's Docket No. 032264-002

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

Thomas J. TAYLOR et al.

Application No.: 10/038,739

Filed: January 2, 2002

For: POLYCARBOXY/POLYOL
FIBERGLASS BINDER

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) Group Art Unit: 1713
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) Examiner: Marie L. Reddick
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) Confirmation No. 3736
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BRIEF FOR APPELLANT

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Sir:

This appeal is from the decision of the Primary Examiner dated June 2, 2003 (Paper No. 6), finally rejecting claims 1, 5, 7, 8 and 10-20, which are reproduced as an Appendix to this brief.

The Director is hereby authorized to charge the \$330.00 government fee and any appropriate fees under 37 C.F.R. §§1.16, 1.17, and 1.21 that may be required by this paper, and to credit any overpayment, to Deposit Account No. 02-4800. Two extra copies of this Brief are being filed herewith and a copy of this page and the signature page are submitted in duplicate.



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I. Real Party in Interest

The present application is assigned to Johns Manville International, Inc.

II. Related Appeals and Interferences

The undersigned legal representative, or assignee, does not know of any other appeal or interferences which will affect or be directly affected by or have bearing on the Board's decision in the pending appeal.

III. Status of Claims

Claims 1, 5, 7, 8 and 10-20 are presently pending and on appeal. No additional amendment was made to the claims after the final rejection of June 2, 2003. The claims under appeal are set forth in the Appendix to this Brief.

IV. Status of Amendments

No amendment was filed after the final rejection of June 2, 2003.

V. Summary of the Invention

The present invention relates to a novel fiberglass binder which comprises a polycarboxy polymer and a polyol. Specifically, the binder relates to a polycarboxy polymer which has a molecular weight of around 5000 or less, and a polyol such as triethanolamine (page 7 of the specification, lines 17-18, and line 30). The use of these binders, with a specified hydroxyl/carboxy ratio in the range of from 0.6 to 0.8 and the low molecular weight, results in few, if any, processing difficulties when preparing a fiberglass product.

Sticking a balling of the fiberglass fibers during the preparation of the fiberglass mat become of minimal concern. The resulting product has also been shown to exhibit excellent recovery and rigidity properties, and surprisingly excellent storage modules within the specified hydroxyl/carboxyl range (page 10 of the specification, lines 11-32, and page 16, lines 3-7).

To achieve the surprising results of the present invention, it is important to use a low molecular binder in a specified hydroxyl/carboxy ratio. Specifically, it has been found that for the molecular weight polycarboxy polymers, where the molecular weight of the polycarboxy polymer is less than 5000, and preferably approaches 2000, the ratio should approach 0.7/1, e.g., is in the range of from 0.6 to 0.8 (page 10 of the specification, lines 20-32, and page 16, lines 3-7 and 22-24). This recognition of the importance of combining such low molecular weight with the specific hydroxyl/carboxyl range is nowhere in the prior art.

VI. The Issues

Issue 1: The first issue under appeal is whether claims 1, 5, 7, 8, 10, 11, 13, 14, 15, 17, 18 and 20 are indefinite under 35 U.S.C. §112 for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention.

Issue 2: The second issue is whether claims 1, 5, 7, 8 and 10-20 are properly rejected under the judicially created doctrine of obviousness-type double patenting as being unpatentable over claims 1-24 of U.S. Patent No. 6,331,350.

Issue 3: The third issue is whether claims 1, 5, 7, 8 and 10-20 are anticipated under 35 U.S.C. §102, or in the alternative, are obvious under 35 U.S.C. §103 over Arkens et al (U.S. Patent No. 5,427,587), Arkens et al (U.S. Patent No. 5,661,213), Arkens et al U.S. Patent No. 5,763,524), Arkens et al (U.S. Patent No. 6,136,916), Chen et al (U.S. Patent No.

6,274,661 B1) or EP 583 068 A1 (Arkens et al).

VII. Grouping of Claims

All claims are to be considered together and would fall or stand together.

VIII. Argument

Issue 1:

The Examiner rejected claims 1, 5, 7, 8 10, 11, 15, 17, 18 and 20 under 35 U.S.C. § 112, second paragraph, for being indefinite. The Examiner rejects the claims due to the recitation of "molecular weight". It is maintained by the Examiner that it is not readily ascertainable as to if "weight average" or "number average" is intended.

The molecular weight is a number average molecular weight. This is noted in Table 1 as Daltons, which method of determining the number average molecular weight is disclosed, for example, in U.S. Patent No. 5,932,665 (copy attached as Appendix B). See in particular, column 4, lines 44-57, and column 8, lines 11-16 of the '665 patent. One skilled in the art would understand that Daltons refers to a method of determining the number average molecular weight in accordance with the industry, e.g., as described in U.S. Patent No. 5,932,665. It is submitted, therefore, that the skilled artisan would understand the intended scope of the claims as written once read in the light of the specification, and viewed in light of the knowledge of the industry.

Issue 2:

Claims 1, 7, 8, and 10-20 stand rejected under the judicially created doctrine of obviousness-type double patenting as being unpatentable over claims 1-24 of U.S. Patent No.

6,331,350 (copy attached in Appendix C).

The claims of the '350 patent specifically recite certain pH ranges. All claims of the '350 patent are specifically delimited by a pH limitation. None of the claims of the subject application contain a pH limitation. The claims of the present application, however, require a specific hydroxyl/carboxy ratio. Therefore, one could easily be covered by the claims of one patent, but not the other. Claim 1 of the '350 patent does not suggest claim 1 of the present application. Indeed, the pH limitation in claim 1 of the '350 patent is not an element in the claims of the subject application. One of ordinary skill in the art would not find it obvious to practice the process of the '350 patent at any suitable pH.

Therefore, it is submitted that the double patenting rejection is improper, and ought to be withdrawn. The issuance of the present application as a patent with its pending claims, would not result in an improper extension of the "right to exclude" since the subject matter claimed in the '350 patent and the subject matter claimed in the subject application are patentably distinct, and cover different subject matter.

Issue 3:

The Examiner rejects the claims under appeal, i.e., claims 1, 5, 7, 8, and 10-20, under 35 U.S.C. § 102(b) or (e), or under 35 U.S.C. § 103(a), over Arkens et al. (U.S. Patent No. 5,427,587); Arkens et al. (U.S. Patent No. 5,661,213); Arkens et al. (U.S. Patent No. 5,763,524); Arkens et al. (U.S. 6,136,916); Chen et al. (U.S. 6,274,661) or EP 583086. The presently claimed invention, however, is not specifically suggested or suggested in the cited prior art. Nor are the advantages of the claimed invention recognized, and thus, the requisite motivation to practice the claimed invention simply does not exist in the prior art.

The present invention relates to a novel fiberglass binder which comprises a

polycarboxy polymer and a polyol. Specifically, the binder relates to a polycarboxy polymer which has a molecular weight of around 5,000 or less, and a polyol such as triethanolamine. The use of these binders, with a specified hydroxyl/carboxy ratio and low molecular weight, results in few, if any, processing difficulties when preparing a fiberglass product. Sticking and balling of the fiberglass fibers during the preparation of the fiberglass mat become of minimal concern. The resulting product has also been shown to exhibit excellent recovery and rigidity properties, as well as storage modules.

The importance of using a low molecular binder and the specified hydroxyl/carboxy ratio is discussed on page 10 on the specification, beginning with line 26. Specifically, it has been found that for the low molecular weight polycarboxy polymers, where the molecular weight of the polycarboxy polymer is less than 5,000, and preferably approaches 2,000, the ratio should approach 0.7/1 for the most advantageous results. This finding is totally unexpected in light of the prior art.

The comparative data in the specification demonstrates the importance of this molecular weight and hydroxyl/carboxy ratio relationship. For example, on page 16 of the specification, it is noted that the lowest molecular weight resin (resin D), which had a molecular weight of 2,000, with a stoichiometry of 70% (ratio of 0.7/1) gave the best acrylic bonded product performance (recovery and group).

Also attached hereto (as Appendix D) is a series of graphs which clearly demonstrate that surprising performance for acrylic resin binders is observed when the hydroxyl/carboxy ratio is in the range of from 0.6 to 0.8, and most particularly about 0.7. The graphs were prepared with an acrylic resin of a molecular weight less than 5,000. This combination of low molecular weight and specific hydroxyl/carboxy ratio, and its importance to maximum

performance, is nowhere disclosed in the prior art.

Furthermore, attached hereto (as Appendix E) is another graph showing the importance of a hydroxyl/carboxyl ratio in the range of from 0.6 to 0.8, one approaching 0.7, for purposes of storage modules. At a molecular weight of 3200 number average molecular weight, the percent triethanolamine employed must be in the range of from 60 to 80% to achieve the best ratio of storage modules to loss modules. The graph was prepared by Diana Fisler of Johns Manville.

The prior art does disclose fiberglass binders which include an acrylic acid polymer and a polyol. Broad ranges for the ratios of equivalents of hydroxyl groups to equivalents of carboxy groups are disclosed in the various references. However, nowhere is there a specific example, or any suggestion that one should employ a molecular weight of less than 5,000 in combination with a hydroxyl/carboxy group equivalents ratio in a range of from 0.6 to 0.8/1. The surprising advantages realized by the presently claimed invention and demonstrated in the attached graphs is nowhere disclosed in the prior art.

Accordingly, there is no anticipation as the specific combination of the low molecular weight polymers and the specific hydroxyl/carboxyl group ratio is nowhere disclosed in the prior art. The claimed subject matter also is not rendered obvious because the surprising results achieved by the combination, as claimed and demonstrated in the attached graphs, are nowhere suggested in the prior art.

As such, it is respectfully submitted that the Arkens et al. '587; Arkens et al. '213; Arkens et al. '524; Arkens et al. '916; Chen et al. '661 and EP 583086 patent references cannot anticipate or render obvious Appellants' claimed invention. None of the references specifically disclose a binder comprised of a polycarboxy polymer having a molecular weight


of 5,000 or less which must be used in combination with a polyol in amounts such that the ratio of equivalents of hydroxyl groups to equivalents of carboxy groups approaches 0.7/1, i.e., in a range of from 0.6/1 to 0.8/1. The advantages of the combination of the low molecular weight together with the narrow range of hydroxyl/carboxy ratio is nowhere disclosed in the prior art. Thus, the requisite motivation to practice Appellants' claimed invention simply does not exist in the prior art, and therefore the prior art cannot render the claimed invention obvious.

IX. Conclusion

In light of the foregoing, appellants respectfully request reversal of the Examiner's §112 rejection, obviousness-type double patenting rejection, and art rejections under 35 U.S.C. §§102 and 103.

Respectfully submitted,

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APPENDIX A

The Appealed Claims

1. A fiberglass binder, comprising an aqueous solution of
 - a) a polycarboxy polymer having a molecular weight of 5,000 or less, and
 - b) a polyol

with the amount of polycarboxy polymer and polyol in the binder being such that the ratio of equivalents of hydroxyl groups to equivalents of carboxy groups is in the range of from 0.6/1 to 0.8/1.

5. The fiberglass binder of claim 1, wherein the molecular weight of the fiberglass binder is about 3000 or less.

7. The fiberglass binder of claim 2, wherein the polyol is triethanolamine.

[The dependency of this claim and its connection to "claim 1" as suggested in the Examiner's June 2, 2003 Office Action, end of paragraph 7, will be effected should the subject rejection be reversed.]

8. The fiberglass binder of claim 1, wherein the polycarboxy polymer comprises a homopolymer or copolymer of polyacrylic acid.

10. The fiberglass binder of claim 1, wherein the ratio is in the range of from about 0.6/1 to about 0.75/1.

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11. The fiberglass binder of claim 1, wherein the ratio of equivalents of hydroxyl group to equivalents of carboxy group is in the range of from about 0.65/1 to about 0.75/1.

12. A fiberglass binder, comprising an aqueous solution of
a polycarboxy polymer which comprises a homopolymer or copolymer of polyacrylic acid, and with the molecular weight of the polyacrylic acid being about 5000 or less,
triethanolamine, and
a catalyst comprised of sodium hypophosphite, sodium phosphite, or mixtures thereof,
with the amount of the polyacrylic acid and triethanolamine being such that the ratio of hydroxyl group to carboxyl group equivalents is in the range of from about 0.65/1 to 0.75/1.

13. The fiberglass binder of claim 12, wherein the molecular weight of the polycarboxy polymer is about 3000 or less.

14. The fiberglass binder of claim 12, wherein the molecular weight of the polycarboxy polymer is about 2000.

15. A fiberglass product comprising a mat of glass fibers containing the binder of claim 1.

16. A fiberglass product comprising a mat of glass fibers containing the binder of claim 12.

17. The fiberglass product of claim 15, wherein the product is building insulation.

18. The fiberglass product of claim 15, wherein the building insulation is insulation for the roof.

19. The fiberglass product of claim 16, wherein the product is building insulation.

20. A process for making a fiberglass fiber mat using a binder, with the binder comprising the fiberglass binder of claim 1.



US005932665A

United States Patent [19]

DePorter et al.

[11] **Patent Number:** 5,932,665[45] **Date of Patent:** Aug. 3, 1999[54] **POLYCARBOXY POLYMER ACID BINDERS
HAVING REDUCED CURE TEMPERATURES**[75] **Inventors:** Craig Donald DePorter, Denver;
Thomas John Taylor, Englewood, both
of Colo.[73] **Assignee:** Johns Manville International, Inc.,
Denver, Colo.[21] **Appl. No.:** 08/796,832[22] **Filed:** Feb. 6, 1997[51] **Int. Cl.⁶** C08F 8/32[52] **U.S. Cl.** 525/381; 428/290; 428/365;
428/375; 525/329.6; 525/380; 525/382;
525/384; 525/385[58] **Field of Search** 428/290, 365,
428/375; 525/380, 381, 382, 384, 385[56] **References Cited****U.S. PATENT DOCUMENTS**

3,658,772 4/1972 Volk et al. .

4,076,691 2/1978 Swift et al. .
5,108,798 4/1992 Guerro et al. .
5,143,582 9/1992 Arkens et al. .
5,318,990 6/1994 Strauss .
5,412,026 5/1995 Holy et al. .**FOREIGN PATENT DOCUMENTS**0583086 7/1992 European Pat. Off. .
0651088 1/1994 European Pat. Off. .*Primary Examiner*—Bernard Lipman*Attorney, Agent, or Firm*—Robert D. Touslee[57] **ABSTRACT**

By carefully adjusting the molecular weight and amounts of methacrylic acid and maleic acid and/or maleic anhydride comonomers in polyacrylic acid-based fiberglass binders, binder-treated fiberglass cured and B-staged product throughput may be maintained at production rates designed for phenol/formaldehyde binders due to the lower thermal requirements for cure as compared to homopolyacrylic acid-based binder systems.

7 Claims, No Drawings

POLYCARBOXY POLYMER ACID BINDERS HAVING REDUCED CURE TEMPERATURES

TECHNICAL FIELD

The subject invention pertains to thermosettable binding resins. More particularly, the subject invention pertains to thermosetting, acrylic acid-based binder resins which cure by crosslinking with a polyfunctional, carboxyl group-reactive curing agent. Such binders are useful as replacements for formaldehyde-based binders in non-woven fiberglass goods.

BACKGROUND ART

Polymeric fiberglass binders have a variety of uses ranging from stiffening applications where the binder is applied to woven or non-woven fiberglass sheet goods and cured, producing a stiffer product; thermoforming applications wherein the binder resin is applied to sheet or lofty fibrous product following which it is dried and optionally B-staged to form an intermediate but yet curable product; and to fully cured systems such as building insulation, wherein the binder is fully cured to its thermoset state while the fiberglass is in the fully expanded condition, following which the rolls or batts are compressed for storage and shipment. In the latter case, it is important that upon releasing the compression, that the batt or roll of fiberglass insulation recover a substantial part of its precompressed thickness.

Polymeric binders used in the present sense should not be confused with matrix resins which are an entirely different and non-analogous field of art. While sometimes termed "binders", matrix resins act to fill the entire interstitial space between fibers, resulting in a dense, fiber reinforced product where the matrix must translate the fiber strength properties to the composite, whereas "binder resins" as used herein are not space-filling, but rather coat only the fibers, and particularly the junctions of fibers. Binder resins in these applications perform no translation of fiber strength. Rather, the unique physical properties of these products are related in general to polymer stiffness rather than fiber strength. Fiberglass binders also cannot be equated with paper or wood product "binders" where the adhesive properties are tailored to the chemical nature of the cellulosic substrates. Many such resins, e.g. urea/formaldehyde and resorcinol/formaldehyde resins, are not suitable for use as fiberglass binders. One skilled in the art of fiberglass binders would not look to cellulosic binders to solve any of the known problems associated with fiberglass binders.

From among the many thermosetting polymers, numerous candidates for suitable thermosetting fiberglass binder resins exist. However, binder-coated fiberglass products are often of the commodity type, and thus cost becomes a driving factor, ruling out such resins as thermosetting polyurethanes, epoxies, and others. Due to their excellent cost/performance ratio, the resins of choice in the past have been phenol/formaldehyde resins. Phenol/formaldehyde resole resins can be economically produced, and can be extended with urea prior to use as a binder in many applications. Such urea-extended phenol/formaldehyde resole binders have been the mainstay of the fiberglass insulation industry for years, for example.

Over the past several decades however, minimization of volatile organic compound emissions (VOCs) both on the part of the industry desiring to provide a cleaner environment, as well as by Federal regulation, has led to extensive investigations into not only reducing emissions from the current formaldehyde-based binders, but also into

candidate replacement binders. For example, subtle changes in the ratios of phenol to formaldehyde in the preparation of the basic phenol/formaldehyde resole resins, changes in catalysts, and addition of different and multiple formaldehyde scavengers, has resulted in considerable improvement in emissions from phenol/formaldehyde binders as compared with the binders previously used. However, with increasingly stringent Federal regulations, more and more attention has been paid to alternative binder systems which are free from formaldehyde.

One such candidate binder system employs polymers of acrylic acid as a first component, and a polyol such as glycerine or a modestly oxyalkylated glycerine as a curing or "crosslinking" component. The preparation and properties of such poly(acrylic acid)-based binders, including information relative to the VOC emissions, and a comparison of binder properties versus urea formaldehyde binders is presented in "Formaldehyde-Free Crosslinking Binders For Non-Wovens", Charles T. Arkins et al., TAPPI JOURNAL, Vol. 78, No. 11, pages 161-168, November 1995. The binders disclosed by the Arkins article, appear to be B-stageable as well as being able to provide physical properties similar to those of urea/formaldehyde resins. Unfortunately, urea/formaldehyde resins do not in general offer the same properties as phenol/formaldehyde resins, the most widely used fiberglass binder resins.

U.S. Pat. No. 4,076,917 discloses β -hydroxyalkylamides, more particularly bis(β -hydroxyalkylamides) as curing agents for polymers containing carboxyl functionality. Numerous unsaturated monomers are disclosed for preparation of the carboxyl-functional polymer, and copolymers of ethylacrylate/methacrylic acid, and ter- and tetrapolymers of butylacrylate/methylmethacrylate/styrene/methacrylic acid; ethylacrylate/styrene/methacrylic acid; butyl acrylate/methacrylic acid/styrene/maleic anhydride; and ethylacrylate/methylmethacrylate/methacrylic acid are among the carboxylic acid group-containing polymers exemplified.

U.S. Pat. No. 5,108,798 discloses water soluble binders prepared from polyfunctional carboxylic acids and β -hydroxyurethanes. Among the polycarboxylic acids, preference is given to monomeric polycarboxylic acids such as the cycloalkane tetracarboxylic acids and anhydrides, pyromellitic acid and its anhydride, and maleic acid and its anhydride. Polymaleic acid and polymaleic anhydride are also identified. Poly(acrylic acids) are exemplified as not producing cured products with good tensile strength.

U.S. Pat. No. 5,143,582 discloses heat resistant non-wovens containing ammonia-neutralized polycarboxylic acids, either monomeric or polymeric, and β -hydroxyalkyl amides. High molecular weight poly(acrylic acid) is shown to be superior to low molecular weight poly(acrylic acid) in these applications. Apparent cure temperature is 204° C. However, the binder compositions are believed to liberate ammonia upon cure. Ammonia emissions are becoming increasingly tightly regulated.

U.S. Pat. No. 5,318,990 discloses fiberglass insulation products cured with a combination of a polycarboxy polymer, a β -hydroxyalkylamide, and an at least trifunctional monomeric carboxylic acid such as citric acid. No polycarboxy polymers other than poly(acrylic acid) are disclosed, although co- and terpolymer polycarboxy acids are broadly disclosed.

Published European Patent Application EP O 583 086 A1 appears to provide details of polyacrylic binders whose cure is catalyzed by a phosphorus-containing catalyst system as

discussed in the Arkens article previously cited. European Published Application EP O 651 088 A1 contains a related disclosure pertaining to cellulosic substrate binders. The fiberglass binders of EP '086 are partially neutralized polycarboxy polymers and hydroxyl-functional curing agents wherein the polycarboxy polymers are prepared in the presence of sodium hypophosphite, incorporating the latter into the polymer structure or by incorporating sodium hypophosphite separately into the curable mixture of polycarboxy polymers to serve as the curing catalyst. Terpolymers of acrylic acid, maleic acid, and sodium hypophosphite are exemplified but appear to reduce both dry and wet tensile strength as compared to poly(acrylic acid) catalyzed with sodium hypophosphite. Higher molecular weight poly(acrylic acids) are stated to provide polymers exhibiting more complete cure. Under the same conditions, copolymers of acrylic acid and maleic acid are shown to have less complete cure as shown by the swell ratios of the polymers, and the copolymer with higher maleic acid content fared worse in this comparison.

Further, and most importantly, as Arkens indicates, the normal cure temperature of the acrylic binder resins is approximately 180° C., and a final cure does not take place without prolonged heating at this temperature or by allowing the temperature to rise to the range of 220° C. to 240° C. The combination of curing temperature and cure time necessitates thermal energy requirements considerably in excess of what is normally desirable for phenol/formaldehyde resins. While it might seem that a simple increase in furnace temperature could provide the additional thermal energy required, it must be remembered that in a commercial setting, the exceptionally large furnaces, powerful heat supplies, and ancillary equipment must all be changed if a binder with higher thermal energy curing requirements is to be used. These changes are not minimal, and represent a considerable financial investment, in many cases requiring significant additional furnace length. Moreover, it is highly likely that for a considerable period of time at least, a variety of binder resins may be used on the same line at different times. Thus, any change made to the curing ovens must be easily reversible. Thus, poly(acrylic acid) binder systems having curing energy requirements similar to those of phenol/formaldehyde binders would be desirable.

The cure temperatures and rates of cure are believed to be dependent upon a number of factors. These, of course, include the reactivity of the carboxylic acid and polyol and the presence and type of esterification catalyst present. The poly(acrylic acid) polymer and the polyol together contain far more theoretical crosslinking possibilities than is believed necessary to provide the necessary crosslinking to attain a thermoset binder. It is believed that a significant fraction of carboxylic acid groups from the poly(acrylic acid) and hydroxyl groups from the polyol in fact do not esterify, but remain unreacted in the thermoset product. One of the reasons for the difficulty of esterification of poly(acrylic acid) carboxylic acid groups and polyol hydroxyl groups is that poly(acrylic acid) is believed to form self-associating discrete phases upon loss of water solvent, possibly to the exclusion of the polyol present. Crosslinking via esterification can then only occur when sufficient thermal energy is present to disrupt these discrete phases. Such molecular disruption may occur solely via thermally-induced molecular motions, and/or by a change in the poly(acrylic acid) molecule caused by internal anhydride formation between neighboring carboxylic acid groups.

SUMMARY OF THE INVENTION

It has now been surprisingly discovered that cure temperatures of polycarboxy polymer binders can be signifi-

cantly lowered through incorporation of maleic acid and/or maleic anhydride into the polycarboxy polymer, and operating on the lower apparent molecular weight end of the 20-100 KDa range. By these methods, curing temperatures can be lowered from c.a. 180° C. to temperatures less than 140° C. As a result, the suitability of polyacrylic acid binders as replacements for phenol/formaldehyde and other formaldehyde-based resins in current commercial operations is enhanced.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a DMA plot illustrating the temperatures associated with the onset and terminus of cure.

FIG. 2 is a DMA plot illustrating a two-step cure.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The polycarboxy polymers useful in the binder systems of the present invention comprise minimally 20 weight percent of polymerized poly(acrylic acid) moieties and at least 10 weight percent of maleic acid and/or maleic anhydride moieties. Other polymerizable monomers, i.e. styrene, acrylonitrile, and the like may also be present. In general, the higher the content of acrylic acid, methacrylic acid, maleic anhydride, and maleic acid, the higher the theoretical crosslink density of the thermosetting resin system. If a resin system with less than the highest degree of crosslinking is desired, non-crosslinkable monomers such as styrene, acrylonitrile, methylacrylate, and methylmethacrylate, may be added. The polymerization of the monomers preferably occurs in aqueous solution, for example by the methods disclosed in U.S. Pat. Nos. 3,658,772 and 5,412,026.

A study was initiated to examine the effects of polymer composition, molecular weight, and polyol and esterification catalyst levels in a series of copolymers and terpolymers produced by the aqueous polymerization of acrylic acid, methacrylic acid, and maleic acid utilizing a free radical polymerization initiator. The polymerizations were carried out at 50% solids and some of the vessels actually were gelled after the polymerization was complete. Although the gels were due to high molecular weight and not crosslinking (they were still soluble), all effects attributed to molecular weight were suspect due to a probable Tromsdorff effect.

Molecular weight determination was done using a Waters HPLC with an Ultrahydrogel linear column (Waters). Water, raised to pH 10 with sodium hydroxide, was employed as the mobile phase. Reported molecular weights are apparent number average molecular weights versus poly(sodium methacrylate) narrow standards (Polysciences) using Millennium 2010 software for data reduction and a linear calibration curve. The molecular weights determined by this method are actually believed to be lower than the actual molecular weights. The term "apparent" used herein and in the claims is reflective of molecular weight measurement as described herein, in other words, at pH 10 versus poly(sodium methacrylate) standards, a method of measurement easily performed by those skilled in the art.

Cure profiles were measured using a Polymer Laboratories, Inc. Model DMTA III Dynamic Mechanical Analyzer (DMA). The binders were impregnated in Whatman microfiberglass filter paper strips, about 0.27 grams of binder solution on two strips about 20 millimeters by 7 millimeters in dimension. The strips were then laminated and clamped into the DMA. Dynamic moduli were measured from 80° C. to 300° C. at 4° C./minute in air. The onset and completion of cure were determined as shown in FIG. 1. The cure evaluations were done in random order.

The cure profiles were characterized by an onset and a terminus of cure. The interpretation of several DMA scans was problematic due to an apparent two-stage cure in many of the formulations containing maleic acid. It was possible, therefore, that some residual free maleic acid monomer was contained in those formulations which contributed to the observed phenomenon. An experiment was conducted to examine the affects of free maleic acid on the cure profile of a polycarboxypolymer/glycerol system. A commercial poly (acrylic acid) was blended with maleic acid at a weight ratio of 1:0.5 and cured with glycerol at a carboxyl:hydroxyl mol ratio of approximately 1:1. DMA showed a two-step cure (FIG. 2) for this system with the first cure being complete at approximately 210° C. followed by a second at 260° C. The poly (acrylic acid) binder cured with glycerol and no maleic acid typically has a cure terminus of approximately 210° C., and it thus appeared that the free residual maleic acid was responsible for further increasing modulus by crosslinking through the unsaturation present. Therefore, when there were two apparent cures in the DMA scan, the first one was considered the "true" cure with respect to analysis of the experimental data.

This study indicated that higher catalyst levels, near stoichiometric polyol, and lower molecular weight favored lower cure temperatures. However, the molecular weight effects were suspect as mentioned earlier.

However, as a result of some of these uncertainties thought present in the first experimental campaign, in a second experimental campaign, a more accurate limitation of molecular weight was achieved through the addition of a chain transfer agent, isopropanol. A potassium persulfate/sodium bisulfite redox-free radical initiator system was

employed. The polymerizations were conducted in septum-sealed 20 mL test tubes with no attempt to deoxygenate reagents or reaction tubes. The correct amount of water for 80 mL of each of the three solvent mixtures was added to a polymerization tube. The initiator was dissolved in the water followed by addition of the chain transfer agent. Sodium bisulfite was then added to the solutions and dissolved. The test tubes were charged with 8 mL of the solvent/initiator/sodium bisulfite mixtures, and the desired monomer amounts added. The tubes were septum sealed and placed into a convection oven at 60° C. ± 5° C. After three hours, the oven was turned off and the tubes allowed to cool to room temperature slowly overnight inside the oven.

The septa were removed from the test tubes and the contents were transferred to scintillation vials. Catalyst and polyol was then added. If necessary, small amounts of methanol were added to reduce viscosity and assist in homogenation. In some cases, the vials were warmed with hot water for the same reason. The curable binder was added to glass fiber filter strips as before. In the second set of polymerizations, the solids content was approximately 20% instead of 50%. As a result of the lower solids content, the viscosity of the polymer solutions were significantly lower than those in the first campaign, and thus, the Tromsdorff effect was not believed operable. In the second campaign, the initiator level was kept constant at 3 parts per 100 parts of monomer (phm), and sodium bisulfite was used as a redox catalyst for the initiator at 1.5 phm. The charges for campaign 2 are presented in Table 1. In the Table, AA is acrylic acid, MA is methacrylic acid, MaA is maleic acid weight fractions as charged, and iPA is isopropanol. The columns identified as X-AA, X-MA, and X-MaA are the inferred polymer compositions in weight fractions, based on analysis of residual, unreacted monomers in the polymerization vials.

TABLE 1

Trial	Run Order ^a	AA	MA	MaA	X-AA	X-MA	X-MaA	iPA ^b	Onset ^c	Final ^c	Mw/Mn	Mn	Mw
1	15	0	0.5	0.5	0	0.659	0.341	50	171	237	2.41	60,000	144,000
2	16	0	0.5	0.5	0	0.619	0.381	125	176	199	2.49	50,000	125,000
3	14	0	0.5	0.5	0	0.610	0.390	200	168	192	2.40	46,000	111,000
4	1	0	1	0	0	1	0	50	174	205	2.36	38,000	89,000
5	17	0	1	0	0	1	0	125	174	207	2.54	26,000	66,000
6	5	0	1	0	0	1	0	200	172	195	2.46	30,000	73,000
7	8	0.5	0	0.5	0.621	0	0.379	50	153	182	2.32	35,000	81,000
8	12	0.5	0	0.5	0.619	0	0.381	125	146	177	2.00	26,000	51,000
9	10	0.5	0	0.5	0.609	0	0.390	200	145	174	2.14	25,000	53,000
10	9	1	0	0	1	0	0	50	144	197	2.48	33,000	81,000
11	11	1	0	0	1	0	0	125	141	200	2.32	26,000	60,000
12	7	1	0	0	1	0	0	200	145	202	2.34	25,000	58,000
13	18	0	0.75	0.25	0	0.527	0.473	50	180	222	2.13	56,000	120,000
14	3	0	0.75	0.25	0	0.550	0.449	125	175	216	2.52	33,000	83,000
15	19	0	0.75	0.25	0	0.552	0.448	200	177	226	2.28	39,000	88,000
16	4	0.75	0	0.25	0.521	0	0.479	50	146	178	2.47	30,000	73,000
17	20	0.75	0	0.25	0.626	0	0.374	125	142	169	2.25	34,000	76,000
18	3	0.75	0	0.25	0.628	0	0.372	200	139	170	2.04	21,000	44,000
19	2	0.5	0.5	0	0.499	0.500	0	50	144	197	2.51	44,000	110,000
20	21	0.5	0.5	0	0.488	0.512	0	125	149	189	2.44	28,000	68,000
21	6	0.5	0.5	0	0.472	0.528	0	200	148	194	2.44	26,000	65,000
22	22	0.25	0.25	0.5	0.379	0.381	0.240	50	150	181	2.53	35,000	88,000
23	23	0.25	0.25	0.5	0.374	0.380	0.245	125	155	181	2.44	31,000	76,000
24	24	0.25	0.25	0.5	0.371	0.381	0.247	200	146	173	2.43	30,000	72,000
25	25	0.375	0.375	0.25	0.350	0.350	0.300	50	152	220	2.59	51,000	131,000
26	26	0.375	0.375	0.25	0.362	0.415	0.222	1	144	168	2.56	33,000	84,000

^aOrder that the DMA experiments were run.

^biPA = 2-propanol used as the chain transfer agent in PHM. Balance of 400 PHM made up water.

^cMeasured onset and terminus of cure, °C.

The polymers were cured with glycerol and sodium hypophosphite hydrate as an esterification catalyst. The onset and completion of cure are shown as measured in Table 1.

TABLE 2

Best Candidates From Predictive Equations (Weight Fractions Monomer as Charged)						
Row	AA	MA	MaA	ipA ^a	Onset ^b	Final ^b
1	0.35	0.15	0.5	200	146	169
2	0.4	0.1	0.5	162	147	169
3	0.4	0.1	0.5	181	145	167
4	0.4	0.1	0.5	200	144	166
5	0.45	0.05	0.5	125	147	169
6	0.45	0.05	0.5	144	146	167
7	0.45	0.05	0.5	162	145	165
8	0.45	0.05	0.5	181	144	164
9	0.45	0.05	0.5	200	142	162
10	0.45	0.1	0.45	162	146	170
11	0.45	0.1	0.45	181	145	169
12	0.45	0.1	0.45	200	143	168
13	0.5	0	0.5	106	146	169
14	0.5	0	0.5	125	145	166
15	0.5	0	0.5	144	145	164
16	0.5	0	0.5	162	144	162
17	0.5	0	0.5	181	142	161
18	0.5	0	0.5	200	141	159
19	0.5	0.05	0.45	144	145	169
20	0.5	0.05	0.45	162	144	167
21	0.5	0.05	0.45	181	143	166
22	0.5	0.05	0.45	200	142	165
23	0.5	0.1	0.4	200	143	170
24	0.55	0	0.45	125	145	168
25	0.55	0	0.45	144	144	166
26	0.55	0	0.45	162	143	164
27	0.55	0	0.45	181	142	163
28	0.55	0	0.45	200	141	162
29	0.55	0.05	0.4	162	144	169
30	0.55	0.05	0.4	181	143	168
31	0.55	0.05	0.4	200	142	168
32	0.6	0	0.4	144	144	168
33	0.6	0	0.4	162	143	167
34	0.6	0	0.4	181	142	166
35	0.6	0	0.4	200	141	166
36	0.65	0	0.35	162	143	170
37	0.65	0	0.35	181	142	169
38	0.65	0	0.35	200	141	169

^aipA = 2-propanol used as chain transfer agent in PHM, balance of 400 PHM water.

^bPredicted onset and terminus of cure, °C.

TABLE 3

Test Points Measured and Predicted Cure Behaviors 200 PHM ipA, Stoichiometric Glycerol, 10 phb Catalyst						
AA	MA	MaA	Onset (°C)		Final (°C)	
(wt. Frac)	(wt. Frac)	(wt. Frac)	Measured	Predicted	Measured	Predicted
0.5	0	0.5	143	141	177	159
0.65	0	0.35	140	141	176	169
0.75	0	0.25	141	141	173	177
0.375	0.375	0.25	146	141	201	186

The results of the heretofore-described experimentation indicate that addition of maleic acid- and/or maleic anhydride-derived moieties to a polycarboxy polymer acid component of a curable binder system is effective in lowering the curing temperature significantly. Without wishing to be bound to any particular theory, applicants believe that the vicinal carboxylic acid groups of maleic acid tend to

prevent or minimize the self-associating discrete phases which poly(acrylic acid) polymers may otherwise adopt, thus increasing the likelihood of esterification without requiring disruption of the inter- and intramolecular order by thermal energy. The effect of maleic acid on cure temperature is far greater than any effect which might be attributed to the number of carboxy groups, a factor which might affect the ultimate crosslink density but should not greatly affect cure temperature.

It has been further discovered that faster cures can be achieved by lowering the molecular weight of the polycarboxy polymers to below about 6×10^4 Da (Daltons), preferably below 5×10^4 Da, and most preferably below 3×10^4 Da relative to poly(sodium methacrylate) standards. Molecular weights expressed herein are apparent number average molecular weights versus poly(sodium methacrylate) standards unless otherwise specified. Limiting the molecular weight of the polymer may be achieved by traditional methods, i.e. through addition of increased levels of initiator and/or chain transfer agent. Suitable chain transfer agents are those generally known to those skilled in the art of vinyl polymerization, e.g. isopropanol, 2-butanol, t-butanol, toluene, n-dodecylmercaptan, trichloriodomethane, and the like. The effect of decreased molecular weight is not as great in lowering curing temperature as the effect of incorporating maleic acid. However, the effect is significant nevertheless. Without wishing to be bound to any particular theory, the effect of decreased molecular weight in lowering cure temperature is believed due to increased molecular mobility.

The polycarboxylic polymers of the subject invention include minimally 20 weight percent acrylic acid, preferably 40-70 weight percent acrylic acid, and most preferably about 55 to 65 weight percent acrylic acid. "Acrylic acid" and other monomers referred to herein in weight percent are the weight percent of monomers reacted relative to total monomers.

The polycarboxylic polymers contain minimally 5 weight percent maleic acid and/or maleic anhydride, preferably from 20 weight percent to about 60 weight percent or more, and more preferably from about 30 weight percent to about 50 weight percent.

The polycarboxylic polymers may contain methacrylic acid in minor quantity. However, the methacrylic acid should be present in not more than 30 weight percent, and regardless of actual amount, should not exceed 70 percent w/w of the amount of acrylic acid utilized.

Most preferably, the polycarboxy polymers are composed substantially of the polymerized residues of acrylic acid, maleic acid and/or maleic anhydride, and optionally methacrylic acid. However, it is also possible to add minor quantities, not to exceed 50 weight percent of the total monomer charge, of one or more non-carboxyl functional molecules, i.e. styrene, α -methylstyrene, p-methylstyrene,

methylmethacrylate, acrylonitrile, and the like. Other unsaturated carboxylic acids and poly(carboxylic acids) may also be used. With respect to additional unsaturated carboxylic acids, i.e. itaconic acid, methylmaleic acid, and the like, the amounts employed may be greater than 50 weight percent of all monomers.

The curing component of the subject modified polycarboxy polymer binders include polyfunctional carboxylic acid- and/or carboxylic acid anhydride-reactive functionalities such as hydroxyl, amino, epoxy, and the like. Preferably, however, the reactive functionality is hydroxyl functionality, i.e. the curing component is a polyol. Suitable polyols include but are not limited to glycerol, triethanolamine, trimethylolpropane, pentaerythritol, sorbitol, tetakis[2-hydroxyalkyl]ethylene diamines, poly(vinyl alcohol), partially hydrolyzed polyvinylacetate, and the like.

The compositions of the subject application in general require a catalyst for cure to occur at relatively low temperature. In the case of cure by esterification with hydroxyl groups, suitable catalysts are the known esterification and transesterification catalysts. Examples are metal naphthenates, cobaltates, vanadates, tertiary amines, etc. A preferred esterification catalyst is an alkali metal hypophosphite. Lists of suitable catalysts may be found in the references previously cited, which are incorporated herein by reference. In the case of other reactive functionalities, i.e. curing with amino-functional compounds to form amide or imide linkages, catalysts which promote amidization or imidization may be employed. Such catalysts are well known to the artisan skilled in amidization and/or imidization reactions.

While the best mode for carrying out the invention has been described in detail, those familiar with the art to which this invention relates will recognize various alternative designs and embodiments for practicing the invention as defined by the following claims.

What is claimed is:

1. A process for increasing the throughput of a polyacrylic acid-based binder-treated fiberglass cured or B-staged product, comprising:

selecting as a binder a modified polyacrylic acid-based binder having moieties derived from acrylic acid and maleic acid and an apparent number average molecular weight of less than 60,000 Da, such that the onset of cure measured by DMA at a temperature ramp of 4° C./min. is below about 155° C. and the terminus of cure measured under the same conditions is less than about 200° C.

2. The process of claim 1 wherein said binder comprises the admixture or curable reaction product thereof of

a) a modified polyacrylic acid polymer comprising from about 30 percent to 100 percent acid-functional monomers selected from the group consisting of:

a)i) about 30 to 85 weight percent acrylic acid,

(a)ii) about 1 to about 20 weight percent methacrylic acid, and

a)iii) about 20 to about 70 weight percent maleic acid and/or maleic anhydride, and

a)iv) mixtures thereof,

said weight percents based on the total moles of acid-functional monomers, any non-acid functional monomers comprising one or more copolymerizable, unsaturated, compatible monomers;

b) one or more polyfunctional, carboxylic acid group-reactive curing agent(s);

c) an effective amount of a catalyst which promotes the reaction between carboxylic acid groups and said carboxylic acid group-reactive curing agent.

3. The process of claim 1 wherein said binder comprises

a) an acid-functional polymer comprising from 30 to 100 percent moieties derived from polymerization of unsaturated monomers selected from the group consisting of:

a)i) from about 35 weight percent to about 75 weight percent acrylic acid-derived moieties,

a)ii) from 0 to about 20 weight percent methacrylic-derived moieties;

a)iii) from 25 weight percent to about 70 weight percent maleic acid-derived moieties and/or maleic anhydride-derived moieties; and

a)iv) mixtures thereof,

with the proviso that at least a)i) and a)iii) must be present, and any non-acid-functional monomers comprise copolymerizable compatible monomers, said weight percents based on the moles of total acid-functional polymer;

b) a curing agent bearing a plurality of reactive functionalities reactive with a carboxylic acid group;

c) an amount of a catalyst effective to catalyze the reaction between said carboxylic acid groups of said acid-functional polymer and said curing agent.

4. The process of claim 3 wherein said acid functional polymer has an apparent number average molecular weight between about 20,000 Da and 60,000 Da.

5. The process of claim 3 wherein said acid functional polymer has an apparent number average molecular weight between about 20,000 Da and 30,000 Da.

6. The process of claim 1, wherein the modified polyacrylic acid-based binder has an apparent number average molecular weight of less than 50,000 Da.

7. The process of claim 1, wherein the modified polyacrylic acid-based binder has an apparent number average molecular weight of less than 30,000 Da.

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US006331350B1

(12) **United States Patent**
Taylor et al.

(10) **Patent No.: US 6,331,350 B1**
(45) **Date of Patent: Dec. 18, 2001**

(54) **POLYCARBOXY/POLYOL FIBERGLASS
BINDER OF LOW PH**

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(58) **Field of Search 525/437, 444;
428/221, 292.1, 293.4, 325**

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(57) **ABSTRACT**

Provided is a fiberglass binder which contains a polycarboxy
polymer and a polyol, with a pH of the binder being no
greater than 3.5. It is further preferred that the polycarboxy
polymer has a molecular weight of less than 10,000, and
more preferably about 5000 or less. The binder also prefer-
ably includes a catalyst which is an alkali metal salt of a
phosphorus polyol is preferably triethanolamine. The binder
also preferably includes a catalyst which is an alkali metal
salt of a phosphorus-containing organic acid. The resultant
binder, particularly when used in preparing fiberglass
products, provides minimal processing difficulties and a
product with excellent recovery and rigidity.

24 Claims, No Drawings

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POLYCARBOXY/POLYOL FIBERGLASS BINDER OF LOW PH

FIELD OF THE INVENTION

The subject invention pertains to polycarboxy polymer binding resins. More particularly, the subject invention pertains to thermosetting, acrylic acid-based binder resins which cure by crosslinking with a poly-functional, carboxyl group-reactive curing agent. Such binders are useful as replacements for formaldehyde-based binders in non-woven fiberglass goods.

BACKGROUND OF THE INVENTION

Fiberglass binders have a variety of uses ranging from stiffening applications where the binder is applied to woven or non-woven fiberglass sheet goods and cured, producing a stiffer product; thermo-forming applications wherein the binder resin is applied to sheet or lofty fibrous product following which it is dried and optionally B-staged to form an intermediate but yet curable product; and to fully cured systems such as building insulation.

Fibrous glass insulation products generally comprise matted glass fibers bonded together by a cured thermoset polymeric material. Molten streams of glass are drawn into fibers of random lengths and blown into a forming chamber where they are randomly deposited as a mat onto a traveling conveyor. The fibers, while in transit in the forming chamber and while still hot from the drawing operation, are sprayed with an aqueous binder. A phenol-formaldehyde binder is currently used throughout the fibrous glass insulation industry. The residual heat from the glass fibers and the flow of air through the fibrous mat during the forming operation are generally sufficient to volatilize the majority to all of the water from the binder, thereby leaving the remaining components of the binder on the fibers as a viscous or semi-viscous high solids liquid. The coated fibrous mat is transferred to a curing oven where heated air, for example, is blown through the mat to cure the binder and rigidly bond the glass fibers together.

Fiberglass binders used in the present sense should not be confused with matrix resins which are an entirely different and non-analogous field of art. While sometimes termed "binders", matrix resins act to fill the entire interstitial space between fibers, resulting in a dense, fiber reinforced product where the matrix must translate the fiber strength properties to the composite, whereas "binder resins" as used herein are not space-filling, but rather coat only the fibers, and particularly the junctions of fibers. Fiberglass binders also cannot be equated with paper or wood product "binders" where the adhesive properties are tailored to the chemical nature of the cellulosic substrates. Many such resins, e.g. urea/formaldehyde and resorcinol/formaldehyde resins, are not suitable for use as fiberglass binders. One skilled in the art of fiberglass binders would not look to cellulosic binders to solve any of the known problems associated with fiberglass binders.

Binders useful in fiberglass insulation products generally require a low viscosity in the uncured state, yet characteristics so as to form a rigid thermoset polymeric mat for the glass fibers when cured. A low binder viscosity in the uncured state is required to allow the mat to be sized correctly. Also, viscous binders tend to be tacky or sticky and hence they lead to accumulation of fiber on the forming chamber walls. This accumulated fiber may later fall onto the mat causing dense areas and product problems. A binder which forms a rigid matrix when cured is required so that a

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finished fiberglass thermal insulation product, when compressed for packaging and shipping, will recover to its specified vertical dimension when installed in a building.

From among the many thermosetting polymers, numerous candidates for suitable thermosetting fiber-glass binder resins exist. However, binder-coated fiberglass products are often of the commodity type, and thus cost becomes a driving factor, generally ruling out such resins as thermosetting polyurethanes, epoxies, and others. Due to their excellent cost/performance ratio, the resins of choice in the past have been phenol/formaldehyde resins. Phenol/formaldehyde resins can be economically produced, and can be extended with urea prior to use as a binder in many applications. Such urea-extended phenol/formaldehyde binders have been the mainstay of the fiberglass insulation industry for years.

Over the past several decades however, minimization of volatile organic compound emissions (VOCs) both on the part of the industry desiring to provide a cleaner environment, as well as by Federal regulation, has led to extensive investigations into not only reducing emissions from the current formaldehyde-based binders, but also into candidate replacement binders. For example, subtle changes in the ratios of phenol to formaldehyde in the preparation of the basic phenol/formaldehyde resole resins, changes in catalysts, and addition of different and multiple formaldehyde scavengers, has resulted in considerable improvement in emissions from phenol/formaldehyde binders as compared with the binders previously used. However, with increasingly stringent Federal regulations, more and more attention has been paid to alternative binder systems which are free from formaldehyde.

One such candidate binder system employs polymers of acrylic acid as a first component, and a polyol such as glycerine or a modestly oxyalkylated glycerine as a curing or "crosslinking" component. The preparation and properties of such poly(acrylic acid)-based binders, including information relative to the VOC emissions, and a comparison of binder properties versus urea formaldehyde binders is presented in "Formaldehyde-Free Crosslinking Binders For Non-Wovens", Charles T. Arkins et al., TAPPI JOURNAL, Vol. 78, No. 11, pages 161-168, November 1995. The binders disclosed by the Arkins article, appear to be B-stageable as well as being able to provide physical properties similar to those of urea/formaldehyde resins. Unfortunately, urea/formaldehyde resins do not in general offer the same properties as phenol/formaldehyde resins, the most widely used fiberglass insulation binder resins.

U.S. Pat. No. 5,340,868 discloses fiberglass insulation products cured with a combination of a polycarboxy polymer, a β -hydroxyalkylamide, and an at least trifunctional monomeric carboxylic acid such as citric acid. The specific polycarboxy polymers disclosed are poly(acrylic acid) polymers.

U.S. Pat. No. 5,318,990 discloses a fibrous glass binder which comprises a polycarboxy polymer, a monomeric trihydric alcohol and a catalyst comprising an alkali metal salt of a phosphorous-containing organic acid.

Published European Patent Application EP 0 583 086 A1 appears to provide details of polyacrylic acid binders whose cure is catalyzed by a phosphorus-containing catalyst system as discussed in the Arkins article previously cited. European Published Application EP 0 651 088 A1 contains a related disclosure pertaining to cellulosic substrate binders. The fiber-glass binders of EP '086 are partially neutralized polycarboxy polymers and hydroxyl-functional curing

agents wherein the polycarboxy polymers are prepared in presence of sodium hypophosphite, incorporating the latter into the polymer structure or by incorporating sodium hypophosphite separately into the curable mixture of polycarboxy polymers to serve as the curing catalyst. Polymers of acrylic acid and maleic acid are exemplified, but appear to reduce both dry and wet tensile strength as compared to poly (acrylic acid) catalyzed with sodium hypophosphite. Higher molecular weight poly(acrylic acids) are stated to provide polymers exhibiting more complete cure. See also U.S. Pat. No. 5,661,213.

Further, as Arkins indicates, the normal cure temperature of the acrylic binder resins is approximately 180° C., and a final cure does not take place without prolonged heating at this temperature or by allowing the temperature to rise to the range of 220° C. to 240° C. The combination of curing temperature and cure time necessitates thermal energy requirements considerably in excess of what is normally desirable for phenol/formaldehyde resins. While it might seem that a simple increase in oven temperature could provide the additional thermal energy required, it must be remembered that in a commercial setting, the exceptionally large ovens, powerful heat supplies, and ancillary equipment must all be changed if a binder with higher thermal energy curing requirements is to be used. These changes are not minimal, and represent a considerable financial investment, in many cases requiring significant additional furnace length. Moreover, it is highly likely that for a considerable period of time at least, a variety of binder resins may be used on the same line at different times. Thus, any change made to the curing ovens must be easily reversible. Thus, poly (acrylic acid) binder systems having curing energy requirements similar to those of phenol/formaldehyde binders would be desirable.

While some polycarboxy polymers have been found useful for making fiberglass insulation products, problems have been observed in the processing of the products. Clumping or sticking of the glass fibers to the inside of the forming chambers during the processing has been one major problem for non-phenol formaldehyde binders. As well, it is important that the final product exhibit the recovery and rigidity necessary to provide a commercially acceptable fiberglass insulation product.

Accordingly, it is an objective of the present invention to provide a non-phenol formaldehyde binder.

Yet another object of the present invention is to provide such a binder which allows one to prepare fiberglass insulation products with minimal processing difficulties.

Still another object of the present invention is to provide a fiberglass insulation product which exhibits good recovery and rigidity, and is formaldehyde-free.

These and other objects of the present invention will become apparent to the skilled artisan upon a review of the following description and the claims appended thereto.

SUMMARY OF THE INVENTION

In accordance with the foregoing objectives, there is provided by the present invention a novel fiberglass binder. The binder of the present invention comprises a polycarboxy polymer and a polyol. It is also preferred that the binder comprises a catalyst, such as an alkaline metal salt of a phosphorus-containing organic acid.

An important aspect of the binder of the present invention is that the pH of the binder system is quite low. In particular, the pH of the binder is no greater than 3.5, and is preferably about 2.5 or less, and most preferably about 2 or less. It is

also preferred that the polycarboxy polymer used in the binder has a very low molecular weight. It is preferred that the molecular weight of the polycarboxy polymer is less than 10000, more preferably less than 5000, and most preferably around 3000 or less, with about 2,000 being advantageous. The use of such a low molecular weight polycarboxy polymer in the binder in combination with the pH of 3 or less, results in a binder which exhibits few, if any, processing difficulties when preparing a fiberglass product and also provides a final product with excellent physical characteristics. Sticking and balling of the fiberglass fibers during the preparation of the fiberglass mat become of minimal concern, and the resulting product also exhibits excellent recovery and rigidity properties.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The polycarboxy polymer used in the binder of the present invention comprises an organic polymer or oligomer containing more than one pendant carboxy group. The polycarboxy polymer may be a homopolymer or copolymer prepared from unsaturated carboxylic acids including but not necessarily limited to, acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, maleic acid, cinnamic acid, 2-methylmaleic acid, itaconic acid, 2-methylitaconic acid, α,β -methyleneglutamic acid, and the like. Alternative, the polycarboxy polymer may be prepared from unsaturated anhydrides including, but not necessarily limited to, maleic anhydride, methacrylic anhydride, and the like, as well as mixtures thereof. Methods for polymerizing these acids and anhydrides are well-known in the chemical art.

The polycarboxy polymer of the present invention may additionally comprise a copolymer of one or more of the aforementioned unsaturated carboxylic acids or anhydrides and one or more vinyl compounds including, but not necessarily limited to, styrene, α -ethylstyrene, acrylonitrile, methacrylonitrile, methyl acrylate, ethyl acrylate, n-butyl acrylate, isobutyl acrylate, methyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, bicyclic methacrylate, vinyl methyl ether, vinyl acetate, and the like. Methods for preparing these copolymers are well-known in the art.

Preferred polycarboxy polymers comprise homopolymers and copolymers of polyacrylic acid. It is particularly preferred that the molecular weight of the polycarboxy polymer, and in particular polyacrylic acid polymer, is less than 10000, more preferably less than 5000, and most preferably about 3000 or less, with about 2000 being advantageous. Combining the low molecular weight polycarboxy polymer with the low pH of the binder results in a final product which exhibits excellent recovery and rigidity.

The formaldehyde-free curable aqueous binder composition of the present invention also contains a polyol containing at least two hydroxyl groups. The polyol must be sufficiently nonvolatile such that it will substantially remain available for reaction with the polyacid in the composition during heating and curing operations. The polyol may be a compound with a molecular weight less than about 1000 bearing at least two hydroxyl groups such as, for example, ethylene glycol, glycerol, pentaerythritol, trimethylol propane, sorbitol, sucrose, glucose, resorcinol, catechol, pyrogallol, glycolated ureas, 1,4-cyclohexane diol, diethanolamine, triethanolamine, and certain reactive polyols such as, for example, β -hydroxyalkylamides such as, for example, bis[N,N-di(β -hydroxyethyl)]adipamide, as may be prepared according to the teachings of U.S. Pat. No. 4,076, 917, hereby incorporated herein by reference, or it may be

an addition polymer containing at least two hydroxyl groups such as, for example, polyvinyl alcohol, partially hydrolyzed polyvinyl acetate, and homopolymers or copolymers of hydroxyethyl (meth) acrylate, hydroxypropyl(meth) acrylate, and the like. The most preferred polyol for the purposes of the present invention is triethanolamine (TEA).

The ratio of the number of equivalents of carboxy, anhydride, or salts thereof of the polyacid to the number of equivalents of hydroxyl in the polyol is from about 1/0.01 to about 1/3. An excess of equivalents of carboxy, anhydride, or salts thereof of the polyacid to the equivalents of hydroxyl in the polyol is preferred. The more preferred ratio of the number of equivalents of carboxy, anhydride, or salts thereof in the polyacid to the number of equivalents of hydroxyl in the polyol is from about 1/0.4 to about 1/1. The most preferred ratio of the number of equivalents of carboxy, anhydride, or salts thereof in the polyacid to the number of equivalents of hydroxyl in the polyol is from about 1/0.6 to about 1/0.8, and most preferably from 1/0.65 to 1/0.75. A low ratio, approaching 0.7:1, has been found to be of particular advantage in the present invention, when combined with a low molecular weight polycarboxy polymer and the low pH binder.

The formaldehyde-free curable aqueous binder composition of the present invention also contains a catalyst. Most preferably, the catalyst is a phosphorous-containing accelerator which may be a compound with a molecular weight less than about 1000 such as, for example, an alkali metal polyphosphate, an alkali metal dihydrogen phosphate, a polyphosphoric acid, and an alkyl phosphinic acid or it may be an oligomer or polymer bearing phosphorous-containing groups such as, for example, addition polymers of acrylic and/or maleic acids formed in the presence of sodium hypophosphite, addition polymers prepared from ethylenically unsaturated monomers in the presence of phosphorous salt chain transfer agents or terminators, and addition polymers containing acid-functional monomer residues such as, for example, copolymerized phosphoethyl methacrylate, and like phosphonic acid esters, and copolymerized vinyl sulfonic acid monomers, and their salts. The phosphorous-containing accelerator may be used at a level of from about 1% to about 40%, by weight based on the combined weight of the polyacid and the polyol. Preferred is a level of phosphorous-containing accelerator of from about 2.5% to about 10%, by weight based on the combined weight of the polyacid and the polyol.

The formaldehyde-free curable aqueous binder composition may contain, in addition, conventional treatment components such as, for example, emulsifiers, pigments, filler, anti-migration aids, curing agents, coalescents, wetting agents, biocides, plasticizers, organosilanes, anti-foaming agents, colorants, waxes, and anti-oxidants.

The formaldehyde-free curable aqueous binder composition may be prepared by admixing the polyacid, the polyol, and the phosphorous-containing accelerator using conventional mixing techniques. In another embodiment, a carboxyl- or anhydride-containing addition polymer and a polyol may be present in the same addition polymer, which addition polymer would contain both carboxyl, anhydride, or salts thereof functionality and hydroxyl functionality. In another embodiment, the salts of the carboxy-group are salts of functional alkanolamines with at least two hydroxyl groups such as, for example, diethanolamine, triethanolamine, dipropanolamine, and di-isopropanolamine. In an additional embodiment, the polyol and the phosphorous-containing accelerator may be present in the same addition polymer, which addition poly-

mer may be mixed with a polyacid. In yet another embodiment the carboxyl- or anhydride-containing addition polymer, the polyol, and the phosphorous-containing accelerator may be present in the same addition polymer. Other embodiments will be apparent to one skilled in the art. As disclosed herein-above, the carboxyl groups of the polyacid may be neutralized to an extent of less than about 35% with a fixed base before, during, or after the mixing to provide the aqueous composition. Neutralization may be partially effected during the formation of the polyacid.

It is important for the purpose of the present invention that the pH of the binder be quite low, e.g., be adjusted by adding a suitable acid such as sulfuric acid. In particular, the pH of the binder should be no greater than 3, is preferably about 2.5 or less, and most preferably about 2 or less. For excellent processing advantages have been discovered when such low pH binders are used, while also providing a product which exhibits excellent recovery and rigidity properties. The processing advantages manifest themselves in reduced accumulation of fiber in the collection box and a reduction in cure temperature. The reduction in cure temperature results in a reduction of the amount of energy needed to cure the binder, and thereby permits, if desired, the use of more water in the binder to obtain many processing benefits.

The formaldehyde-free curable aqueous composition may be applied to a nonwoven by conventional techniques such as, for example, air or airless spraying, padding, saturating, roll coating, curtain coating, beater deposition, coagulation, or the like.

The waterborne formaldehyde-free composition, after it is applied to a nonwoven, is heated to effect drying and curing. The duration and temperature of heating will affect the rate of drying, processability and handleability, and property development of the treated substrate. Heat treatment at about 120° C., to about 400° C., for a period of time between about 3 seconds to about 15 minutes may be carried out; treatment at about 150° C., to about 250° C., is preferred. The drying and curing functions may be effected in two or more distinct steps, if desired. For example, the composition may be first heated at a temperature and for a time sufficient to substantially dry but not to substantially cure the composition and then heated for a second time at a higher temperature and/or for a longer period of time to effect curing. Such a procedure, referred to as "B-staging", may be used to provide binder-treated nonwoven, for example, in roll form, which may at a later stage be cured, with or without forming or molding into a particular configuration, concurrent with the curing process.

More particularly, in the preparation of fiberglass insulation products, the products can be prepared using conventional techniques. As is well known, a porous mat of fibrous glass can be produced by fiberizing molten glass and immediately forming a fibrous glass mat on a moving conveyor. The expanded mat is then conveyed to and through a curing oven wherein heated air is passed through the mat to cure the resin. The mat is slightly compressed to give the finished product a predetermined thickness and surface finish. Typically, the curing oven is operated at a temperature from about 150° C. to about 325° C. Preferably, the temperature ranges from about 180° to about 250° C. Generally, the mat resides within the oven for a period of time from about ½ minute to about 3 minutes. For the manufacture of conventional thermal or acoustical insulation products, the time ranges from about 1 minute to about 2½ minutes. The fibrous glass, having a cured, rigid binder matrix, emerges from the oven in the form of a bat which may be compressed for packaging and shipping and which will thereafter substantially recover its vertical dimension when unconstrained.

The heat-resistant nonwovens may be used for applications such as, for example, insulation batts or rolls, as reinforcing mat for roofing or flooring applications, as roving, as microglass-based substrate for printed circuit boards or battery separators, as filter stock, as tape stock, as tape board for office petitions, in duct liners or duct board, and as reinforcement scrim in cementitious and non-cementitious coatings for masonry.

EXAMPLE

A list of resins applied and their properties is shown in Table 1. The resins were inline mixed with a solution containing a yellow dye and an appropriate quantity of an amino silane (OSi A1101), and a soft water stream. These components were then delivered to six sets of twelve spraying nozzles where they were hydraulically dispersed. The nozzles were arranged in six circles spraying the binders towards the center of the freshly formed fiberglass from a distance of about 8 inches. The fiberglass was manufactured using a standard fiberglass spinning machine located approximately 12 inches above each circle of nozzles. The fiberglass production and binder spray rates were kept constant such that the final cured binder content represented about 5.5 weight % of the finished product. Of that cured binder content approximately 0.2% represented the silane. The final solids content of the binders as sprayed was around 10%.

Mat moistures at the end of the forming chamber were measured for each set point (Table 2). This gives a gauge of the dry down rate of each binder. High ramp moisture has been linked to improved product performance.

Binder flow was increased until some signs of under-cure showed up and then slightly reduced. Ramp moistures were measured in excess of 5% when problems were encountered.

The recoveries and droops for each of the samples were analyzed with a two tailed t-test in which early set points were compared to the early control and later set points were compared to the later control. The controls were also compared to determine whether any changes had occurred during the day. Where a significant difference exists (95% confidence), it is indicated with a plus or minus. The results are shown in Table 3.

The results indicate that in almost every set of testing for droop and recovery, upper and lower level, the exit control was consistently worse than the entrance control. Quick product testing results showed little difference in droop or recovery between controls and acrylic resin product on the lower level. Longer term testing reveals lower recoveries for most acrylic binders vs. controls and mixed results for droop on the lower level. Nearly all of the acrylic set points show lower recovery than phenolic controls on the upper level. At the same time nearly all acrylic binders give better droop on the upper level until three months where droop results are mixed. Even at three months there are very few recovery failures and most droop numbers are between 3 and 4.5.

The three molecular weight variants tested had much different behavior in the collection box. In general, the higher the molecular weight, the more collection box buildup resulting in high density uncured spots in the blanket. There was no apparent correlation between TEA stoichiometry or pH and collection box buildup. There are no observable differences in droops or lower level recoveries amongst the various molecular weights.

Generally, there are no significant differences in recovery or droop between TEA levels on the lower level product. Upper level recoveries and droops indicate better product

performance with the higher TEA level for both resins B and D. In theory, the shorter polymer chains require more crosslinks to achieve the same mechanical properties as longer chain polymers with fewer crosslinks. Laboratory studies of crosslinker stoichiometry vs. mechanical strength of the binder indicate this to be true. A crosslinker level of 70% stoichiometry should be used with these low molecular weight acrylic resins.

One polymer system (Resin D, 2100 Dalton M.W.) was trialed at a low pH. The delivered resins had pHs in the range of 3.9–4.2. Sulfuric acid was added to a tote of resin D to produce a resin of pH 3.2 (however, due to a shortage of H₂SO₄, a finished binder pH of 3.5 was achieved). This binder consistently gave the best droop results on both the upper and lower level for all binders throughout the testing period. While there were no significant differences in recoveries between acrylic binders on the lower level, this low pH binder gave consistently better recovery on the upper level when compared to the same binder at a standard pH. Product made with this binder still passes recovery at three months (6.3" upper and lower) with a lower level droop of 3.66" and an upper level droop of 3.03". Corrosion testing (ASTM C665) was performed on the low pH finished product and it passed all tests (steel, copper and aluminum).

Additionally, when reduced to pH=2.0, we found viscosity to be about one-half that of polyacrylic acid of pH=3.8–4.2. Further, when TEA stoichiometry is increased to at least 45%, reduction in viscosity is observed. Reduction of viscosity is greatly desirable in an insulation binder, from a processing perspective. Reduced pH also showed a reduction in cure temperature, by as much as 20° C. While not limiting the invention to any particular theory, we believe the added acid may act as a cure catalyst. Table 4 sets forth cure data. Therefore, the improved binder compositions of the present invention are quite desirable.

From the results, it can be concluded that building insulation can be produced with acrylic resins that are essentially emission free and formaldehyde free. This product can be produced to meet recovery specifications and have equal or better droop than standard phenolic product.

Within the family of acrylic resins (available from Rohm and Haas) the lower molecular weights present fewer processing difficulties. Collection box fiber accumulation is reduced with these acrylic variants. High binder flow rates are still beneficial to product performance. Material handling and pumping of the low molecular weight products are improved over resin A (10,000 Daltons M.W.), especially in cold weather. The lowest molecular weight resin (resin D) with higher TEA stoichiometry (70%) and lower pH (2.5) give the best acrylic bonded product performance (recovery and droop).

TABLE 1

Resin Properties				
Resin	% Solids	Molecular Weight	TEA Stoichiometry	Viscosity (25° C., 40%)
A	40%	10000 Daltons	45%	240 cP
B	51%	4500 Daltons	45%	100 cP
C	45%	3500 Daltons	45%	60 cP

TABLE 1-continued

Resin Properties				
Resin	% Solids	Molecular Weight	TEA Stoichiometry	Viscosity (25° C., 40%)
D	41%	2100 Daltons	55%	20 cP
Phenolic	48%	1000 Daltons	NA	4 cP

TABLE 2

Let-Down Ramp Moistures Let-Down Chain Moistures				
Sample No.				
Test Point	1 % Moisture	2 % Moisture	3 % Moisture	Average % Moisture
0	2.82%	2.79%	2.32%	2.64%
X1	0.89%	0.90%	0.89%	0.89%
X2	2.03%	2.41%	1.60%	2.01%
X2B	5.74%	8.08%	3.20%	5.67%
X4	2.56%	3.51%	2.15%	2.74%
X3	1.84%	3.03%	2.18%	2.35%
X5	4.41%	5.97%	3.20%	4.53%
X7	4.42%	2.88%	4.01%	3.77%
X8	3.83%	3.92%	2.79%	3.51%
X11	2.52%	2.75%	1.77%	2.35%
T1	7.04%	6.59%	9.72%	7.78%
T2A	5.86%	6.96%	10.24%	7.69%
T2B	4.10%	4.73%	5.33%	4.72%

TABLE 3

Product Performance Data Product Performance Results									
Binder	set-point	upper level re-covery	upper level droop	lower level re-covery	lower level droop	Quick			
Phenolic Control	X1	7.44	0	2.73	0	7.02	0	1.98	0
Phenolic Control	X11	7.25	-	3.08	0	6.83	-	2.67	-
Resin D/55% TEA	X2	6.48	-	2.68	0	6.99	0	2.56	-
Resin D/55% TEA	X2B	6.88	-	1.53	+	6.96	0	2.02	0
Resin D/70% TEA	X3	6.89	-	1.71	+	7.00	0	1.98	0
Resin D/55% TEA/pH = 3.2	X4	6.93	-	1.60	+	6.93	0	1.73	0
Resin C/45% TEA	X5	6.95	-	2.00	+	6.94	+	1.94	+
Resin B/45% TEA	X7	7.08	0	1.86	+	6.93	0	1.94	+
Resin B/70% TEA	X8	7.13	-	1.65	+	6.92	0	2.10	+
One Week									
Phenolic Control	X1	7.21	0	3.62	0	6.93	0	3.06	0
Phenolic Control	X11	6.82	-	3.84	0	6.52	-	3.96	-
Resin D/55% TEA	X2	6.52	-	3.14	0	6.60	-	3.79	-
Resin D/55% TEA	X2B	6.34	-	2.73	0	6.55	-	2.54	+

TABLE 3-continued

Product Performance Data Product Performance Results									
Binder	set-point	upper level re-covery	upper level droop	lower level re-covery	lower level droop	One Month			
Resin D/70% TEA	X3	6.67	-	2.14	+	6.58	-	3.42	-
Resin D/55% TEA/pH = 3.2	X4	6.67	-	2.40	+	6.53	-	2.54	+
Resin C/45% TEA	X5	6.54	2.68	6.19	-	3.96	0		
Resin B/45% TEA	X7	6.48	2.94	6.42	0	3.12	+		
Resin B/70% TEA	X8	6.78	2.30	6.51	0	3.29	+		
Three Month									
Phenolic Control	X1	7.03	3.97	6.86	0	3.17			
Phenolic Control	X11	6.84	4.51	6.59	-	4.77	-		
Resin D/55% TEA	X2	6.12	4.52	6.59	-	4.37	-		
Resin D/55% TEA	X2B	6.09	3.18	6.57	-	3.21	0		
Resin D/70% TEA	X3	6.32	3.29	6.55	-	3.64	-		
Resin D/55% TEA/pH = 3.2	X4	6.42	2.68	6.49	-	2.96	0		
Resin C/45% TEA	X5	6.35	3.46	6.33	-	3.95	+		
Resin B/45% TEA	X7	6.25	3.48	6.45	0	3.31	+		
Resin B/70% TEA	X8	6.50	2.82	6.38	-	3.83	0		
Three Month									
Phenolic Control	X1	7.05	3.47	6.67	0	3.50	0		
Phenolic Control	X11	6.65	5.26	6.38	-	5.08	-		
Resin D/55% TEA	X2	6.25	4.51	6.42	-	5.19	-		
Resin D/55% TEA	X2B	5.96	4.60	6.22	-	4.27	0		
Resin D/70% TEA	X3	6.23	3.40	6.25	-	4.71	-		
Resin D/55% TEA/pH = 3.2	X4	6.32	3.03	6.30	-	3.66	0		
Resin C/45% TEA	X5	6.29	3.91	6.20	-	4.00	+		
Resin B/45% TEA	X7	6.23	3.75	6.29	0	4.04	+		
Resin B/70% TEA	X8	6.46	3.33	6.01	-	5.44	0		
+, 0, - stand for better, same, worse than control respectively (95% confidence) all measurements are in inches									
TABLE 4									
RESIN	% TEA	CURE ONSET	IN-FLEC-TION	FI-NAL T	STIFF-NESS	TAN DELTA	MW		
2100 (Ph2)	45	154.9	171.9	188	1.6	0.1075	2100		
2100	45	162.8	181.7	201.6	1.57	0.116	2100		
2100	55	168.8	185.9	202.2	1.72	0.064	2100		

TABLE 4-continued

RESIN	% TEA	CURE ONSET	IN- FLEC- TION	FI- NAL T	STIFF- NESS	TAN DELTA	MW
2100	65	170.5	188.8	205.8	1.74	0.04	2100
1476 (pH2)	45	136.6	154.7	173.5	1.62	0.0836	3500
1476	45	167.9	185.2	203	1.54	0.075	3500
1476	55	168.9	184.7	201.3	1.67	0.048	3500
1476	65	165.4	186	206.1	1.79	0.033	3500
4500 (pH2)	45	148.4	164.4	180.4	1.65	0.0882	4500
4500	45	171.3	185.5	199.7	1.22	0.08	4500
4500	55	170.2	193.1	215.5	1.9	0.057	4500
4500	65	173.2	190.4	210.9	1.78	0.048	4500
HF05 (pH2)	45	142.3	162	181	1.67	0.0918	10000
HF05	45	170.5	187.8	205.8	1.78	0.034	10000
HF05	55	172.1	187	203	1.84	0.04	10000
HF05	65	173	190.2	211.4	1.93	0.027	10000
HF05/ SHP	55	170.6	185.7	200.3	1.51	0.04	10000
HF05- NOSH	55	186.1	206.4	229.6	1.43	0.033	10000

While the invention has been described with preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and the scope of the claims appended hereto.

What is claimed is:

1. The fiberglass binder, comprising an aqueous solution of

a polycarboxy polymer having a number average base molecular weight of less than 5,000, and

a polyol,
with the pH of the binder being no greater than 3.5.

2. The fiberglass binder of claim 1, wherein the binder pH is no greater than 2.5.

3. The fiberglass binder of claim 1, wherein the binder further comprises a catalyst which comprises an alkali metal salt of a phosphorus-containing organic acid.

4. The fiberglass binder of claim 1, wherein the number average based molecular weight of the polycarboxy polymer is less than 3000.

5. The fiberglass binder of claim 1, wherein the number average based molecular weight of the polycarboxy polymer is less than 2000.

6. The fiberglass binder of claim 1, wherein the catalyst is sodium hypophosphite, sodium phosphite, or a mixture thereof.

7. The fiberglass binder of claim 1, wherein the polyol is triethanolamine.

8. The fiberglass binder of claim 1, wherein the polycarboxy polymer comprises a homopolymer or copolymer of polyacrylic acid.

9. The fiberglass binder of claim 1, wherein the amount of polycarboxy polymer and polyol in the binder is such that

the ratio of carboxy group equivalents to hydroxyl group equivalents is in the range of from about 1/0.65 to 1/0.75.

10. A fiberglass binder, comprising an aqueous solution of a homopolymer or copolymer of polyacrylic acid, where the polyacrylic acid polymer has a number average based molecular weight of 5000 or less,

triethanolamine,
with the pH of the binder being no greater than 3.5.

11. The fiberglass binder of claim 10, wherein the pH of the binder is no greater than 2.5.

12. The fiberglass binder of claim 10, wherein the binder further contains a catalyst which comprises an alkali metal salt of a phosphorus-containing organic acid.

13. The fiberglass binder of claim 10, wherein the amount of polyacrylic acid polymer and triethanolamine in the binder is such that the ratio of carboxy group equivalents to hydroxyl group equivalents is in the range of from about 1/0.65 to 1/0.75.

14. A fiberglass binder comprising an aqueous solution of polyacrylic acid polymer having a number average based molecular weight of less than 5000,

triethanolamine,
a catalyst comprising sodium hypophosphite, sodium phosphite or a mixture thereof,

with the pH of the binder being no greater than 3.5 and the amount of polyacrylic acid and triethanolamine in the binder being such that the ratio of carboxy group equivalents to hydroxyl group equivalents is in the range of from about 1/0.65 to 1/0.75.

15. A fiberglass product comprising a mat of glass fibers containing the binder of claim 1.

16. A fiberglass product comprising a mat of glass fibers containing the binder of claim 10.

17. The fiberglass product of claim 15, wherein the product is building insulation.

18. The fiberglass product of claim 16, wherein the product is building insulation.

19. A process for making a fiberglass mat comprising fiberizing molten glass and forming a fibrous glass mat using a binder, with the binder comprising the fiberglass binder of claim 1.

20. The fiberglass binder of claim 1, wherein the binder further comprises an inorganic acid.

21. A fiberglass binder of claim 20, wherein the inorganic acid is sulfuric acid.

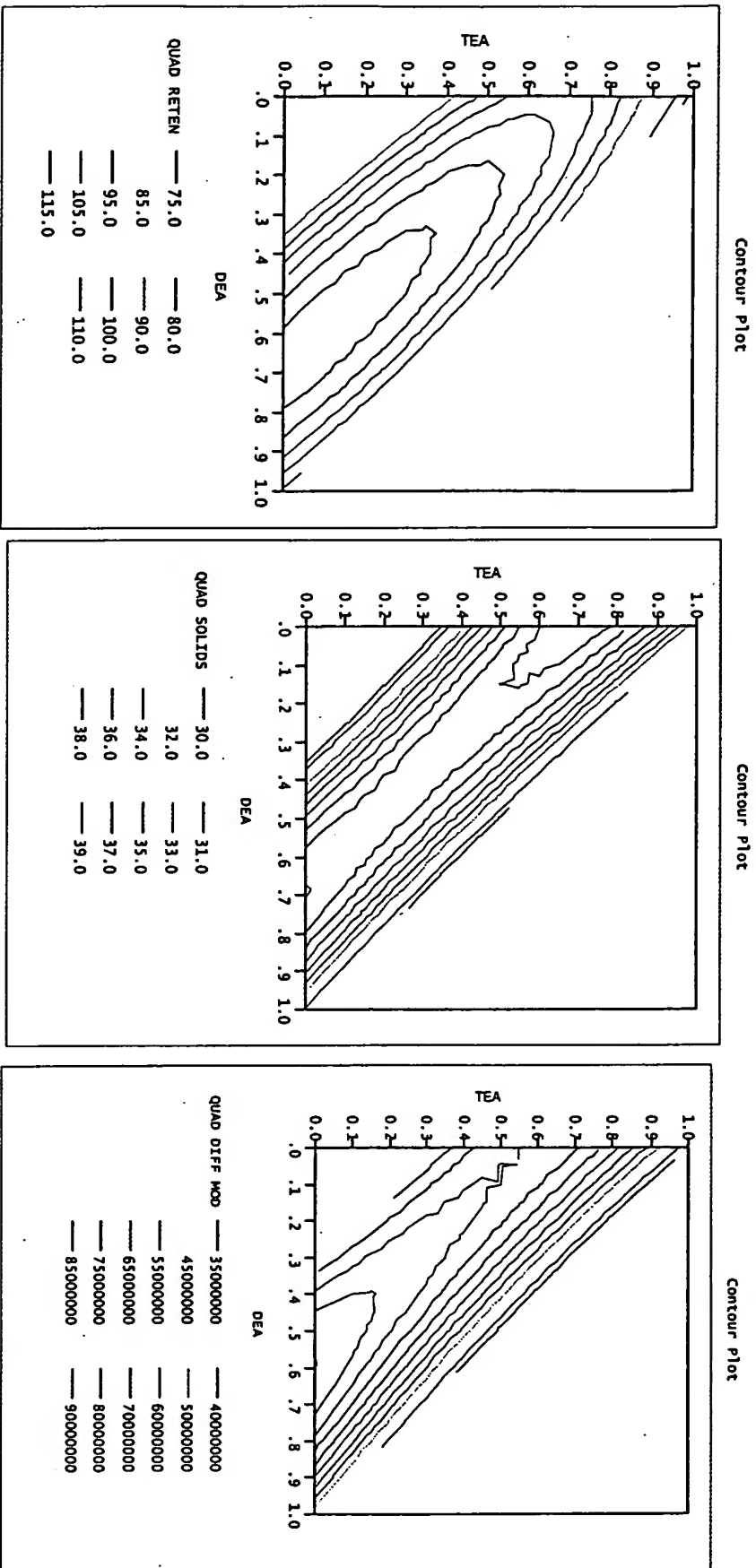
22. A method for preparing the fiberglass binder of claim 1, which comprises preparing an aqueous solution of a polycarboxy polymer, a polyol and an inorganic acid, with the inorganic acid being added in an amount sufficient such that the pH of the fiberglass binder is no greater than 3.5.

23. The method of claim 22, wherein the amount of inorganic acid present is sufficient such that the binder pH is no greater than 2.5.

24. The method of claim 22, wherein the inorganic acid is sulfuric acid.

* * * * *

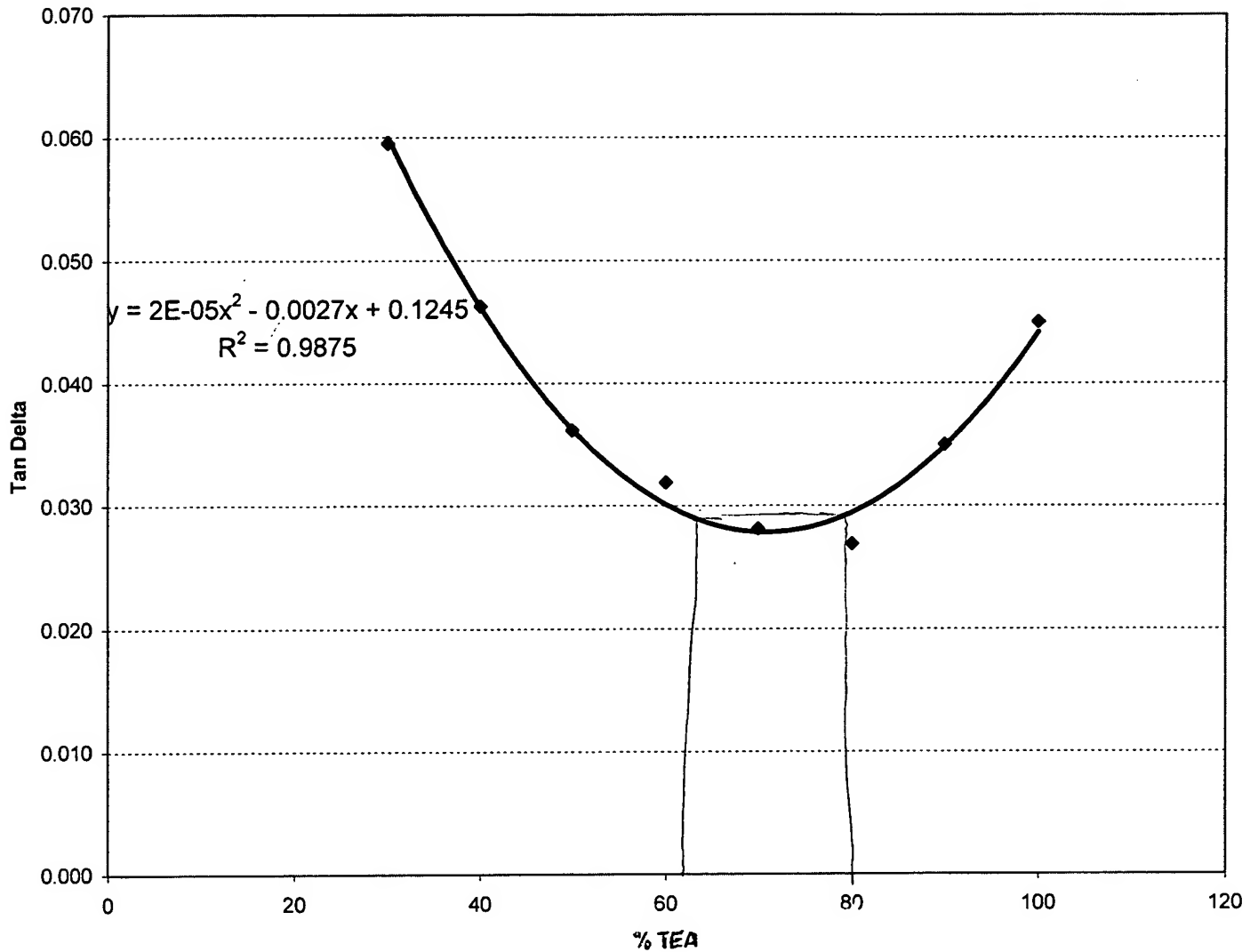
Product Performance vs. TEA and DEA



3200 M.W.

Chart Title

ratio of storage modulus to loss modulus,



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